Journal of Environmental Sciences Vol.16, No.1, pp.145—148, 2004

ISSN 1001—0742
CN11—2629/X

Article ID: 1001-0742(2004)01-0145-04 **CLC number**: X12 **Document code**: A

OH radicals generated by DC corona discharge for improving the pulsed discharge desulfuration efficiency

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Abstract: Positive DC corona discharge is formed with needle-plate electrode configuration, in which the water vapor is ejected though the needle points. The purpose is to increase the numbers of the water-based radicals, ionize the water molecule and improve the desulfuration efficiency of pulsed corona reactor. The water ions were determined by four stages molecular beam mass spectrometer and diagnose the water-based radicals by emission spectrograph. A conclusion on formation of ions and radicals with DC corona discharges can be drawn.

Keywords: DC corona; activator; desulfuration

Introduction

Non-thermal plasma produced by pulsed corona discharge used for flue gas desulphuration has been proved as a promising technique. It was developed in the past 20 years and was one of the newly developed competitive dry methods used to desulfurate (Masuda 1988). Compared with the wet methods, it has such advantages of smaller occupying land area, having no secondary pollution, that the by-products of both removing SO_2 and dusts can be used as fertilizer as well as both dedust and $DeSO_2$ can be achieved simultaneous, which make it a promising technology. Many researches have previously carried out the relative experiments in the lab and many valuable results achieved (Dinelli, 1990; Mizuno, 1986; Chang, 1994; Wu, 1998).

This method utilizes mainly radicals produced by the collision between the high-energy electrons (5—20 eV) in the pulsed corona discharge plasma and the molecules to oxidize the SO_2. H_2SO_4 and $(NH_4)_2SO_4$ will be formed at the presence of water and ammonia.

Water molecules play an important roll in the desulfuration technology, for that active radicals produced by water molecules during the discharge process act as the main useful reactants, which oxidize the SO_2 and $(NH_4)_2SO_3$ into SO_3 and $(NH_4)_2SO_4$. Traditional methods of $DeSO_2$ by the pulsed corona discharge usually adjust the water contained in the flue gas to increase the HO and HO_2 production, and that leads to the increase SO_2 removal.

Some results we have been get: when the needle-plate electrode system was assembled in front of the pulsed corona plasma reactor, the water based radicals ejecting with DC corona discharges can increase the desulfuration efficiency of pulsed corona plasma 10%, and general desulfuration efficiency can get to 90% (Li, 2000; 2001).

In this study, a needle-plate electrode was used. Water vapor was first sprayed out from the tip of the needle, and then passed through the region where there was a large amount of high-energized electrons, thus the collisions probability of electrons and water molecules were greatly increased. Production of active water-based radicals and the ionization of water molecules were thus improved and a better $DeSO_2$ rate achieved.

1 Experimental

The schematic of a diagnosis apparatus for molecular beam mass spectrograph is shown in Fig. 1. Activation electrode is needle-plate electrode configuration. The discharge electrode use stainless steel pipe which external diameter is 1.5 mm, internal diameter is 0.8 mm. The low voltage electrode is the plate with fine hole for skimmer of mass spectrograph. N_2 is bubbled into needle electrode, spurted out and activated. Ions produced are measured by quadrupole mass spectrometer (QMS). The weak signal from the secondary electron multiplier of the QMS is amplifies first and then accumulated over multimass scans using a digital oscilloscope. Discharge voltage is measured by EP-100K probe and digital oscilloscope.

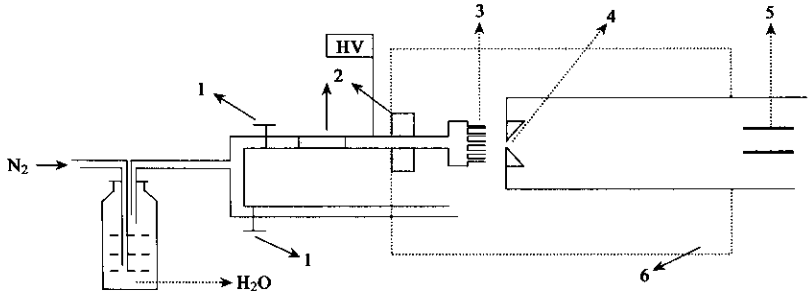

Fig. 1 The schematic of a diagnosis apparatus for molecular beam mass spectrograph
1. needle valve; 2. insulator; 3. needle electrode; 4. fine hole for sampling; 5. four stages mass spectrometer; 6. reaction chamber

Foundation item: 863 High-Tech Project of the National Science and Technology Committee of China (No. 2001AA642010)

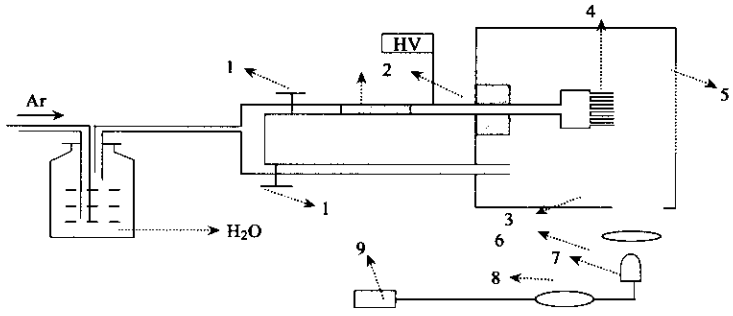

Fig.2 The schematic of emission spectrometry diagnosis
1. needle valve; 2. insulator; 3. discharge chamber; 4. needle electrode; 5. low-voltage net electrode; 6. lens; 7. optical fiber; 8. optical spectrometer; 9. computer

The schematic of emission spectrometry diagnosis is shown in Fig. 2. Optical emission spectrometry (OES) is made in Acton Research Cooperation, whose model is SP-305. Measure wavelength range is 200—1000 nm, the highest resolution is 0.1 nm. The activation electrode use stainless steel duct whose external diameter is 1.5 mm, internal diameter is 0.8 mm. The low voltage use stainless steel net with mesh 2 mm × 2 mm. Light emitted by corona discharge is focused into optical fiber through a convex with Φ25 (f38), input computer and sampled. Argon is bubbled into needle electrode, spurted out and activated by corona discharge. Free radicals produced are measured by spectrometer.

2 Results and discussion

2.1 Diagnoses of the ions

Work voltage is 8 kV, needle-plate spacing is 2 cm in this experiment. Fig. 3 shows the ion mass spectrometer curve of the discharge. As can be seen in the Fig.3, H_2O^+ is produced after the DC discharge of the water molecule. H_2O^+ is the main reactant to generate OH radicals.

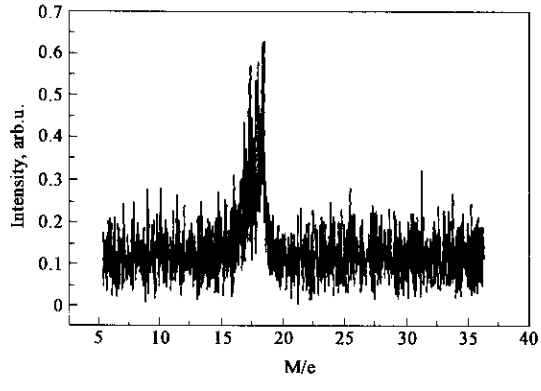

Fig.3 A spectrogram of discharge activation for water molecule

Table 1 Species detected in OH and N_2 DC corona discharges (Ershov, 1995)

Species	Wavelength, nm	Transition
OH	309	$A^2\Sigma \rightarrow X^2\Pi, V = 0 \rightarrow V = 0$
OH	314	$A^2\Sigma \rightarrow X^2\Pi, V = 1 \rightarrow V = 1$
N_2	316	$C^3\Pi \rightarrow B^3\Pi, V = 1 \rightarrow V = 0$

2.2 Diagnoses of the radicals

Fig.4 shows the OH spectrograms of the water molecules (passing through the needle or not) are shown. From the spectrograms, we can see that light intensity of the OH spectrogram is obviously strengthened after the corona discharge.

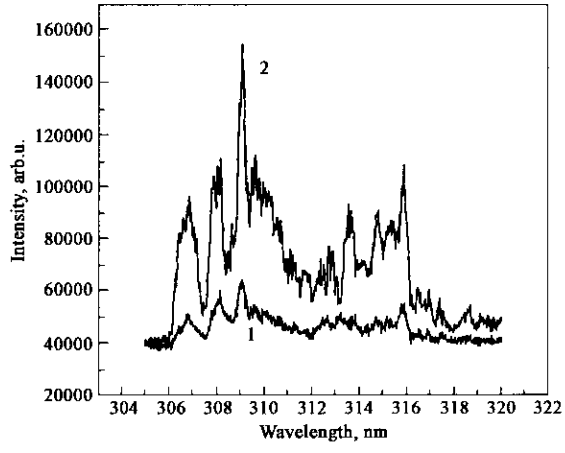

Fig.4 The emissive spectrogram before or after activating water molecule
1. water molecule do not pass through the discharge electrode; 2. water molecule pass through the discharge electrode

OH light intensity of the spectrogram is plotted versus the applied voltage in Fig.5. OH and N_2 DC corona discharge main mechanisms of species detected are shown in Table 5.

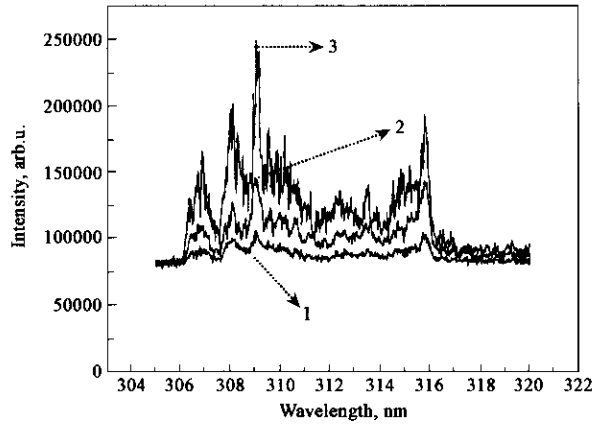

Fig.5 Emissive spectrogram of discharge activation for water molecule
1. 7 kV; 2. 8 kV; 3. 9 kV

Fig. 6 shows the measure results of optical spectrometer under different gas flux. As the gas flux increase, the spectrum curve intensity of 308 nm and 314 nm become stronger. That shows the number of OH

free radicals to increase with enhancing the injection quantity of water.

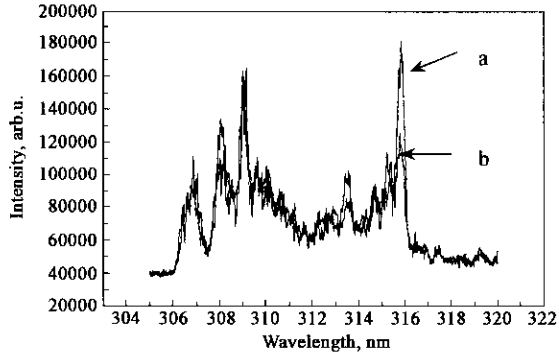

Fig.6 Emissive spectrogram of vapor flow for water molecule
a. 2.0 L/min; b. 1.0 L/min; the activation voltage is 8 kV; needle-plate spacing is 2 cm

2.3 Formation of water-based radicals and their functions on $DeSO_2$

Water-based radicals mainly include HO, HO_2 and H_2O_2 and so on, among which the HO radical has the highest oxidization potential (amount to 2.8 V). Relative reactions of the formation of water-based radical are shown in Table 2.

Table 2 Some reactions and their rate constants(Busi, 1985; Mok, 1998)

No.	Reactions	Rate constants, $m^3/(mol \cdot s)$
R(1)	$H_2O + e^- \rightarrow OH + H + e^-$	3.3×10^{-19}
R(2)	$H_2O + e^- \rightarrow H_2O^+ + 2e^-$	
R(3)	$N^{2+} + H_2O \rightarrow H_2O^+ + N_2$	1.4×10^{-21}
R(4)	$H_2O + H_2O^+ + e^- \rightarrow H_3O^+ + OH + e^-$	7.2×10^{-20}
R(5)	$O + HO_2 \rightarrow O_2 + OH$	$2.9 \times 10^{-21} \exp(200/T)$
R(6)	$H + O_3 + M \rightarrow O_2 + OH + M$	$1.4 \times 10^{-19} \exp(-480/T)$
R(7)	$OH + OH + M \rightarrow H_2O_2 + M$	$6.5 \times 10^{-40} (T/300)^{-0.7}$
R(8)	$OH + H_2O_2 \rightarrow HO_2 + H_2O$	2×10^{-21}
R(9)	$OH + O_3 \rightarrow HO_2 + O_2$	$1.3 \times 10^{-21} \exp(-956/T)$
R(10)	$OH + HO_2 \rightarrow O_2 + H_2O$	$4.8 \times 10^{-20} \exp(250/T)$
R(11)	$H_2O + e^- \rightarrow OH + H^-$	7.2×10^{-20}
R(12)	$OH + OH \rightarrow H_2O + O$	2×10^{-21}

Table 3 OH radicals $DeSO_2$ reaction and the rate constants in gas phase (Chang, 1988; Dahiya, 1993; Lowke, 1995; Mueller, 2000)

No.	Reactions	Rate constants, $m^3/(mol \cdot s)$
R(13)	$SO_2 + OH \rightarrow HSO_3$	7.5×10^{-21}
R(14)	$OH + HSO_3 \rightarrow H_2SO_4$	1.0×10^{-21}
R(15)	$O + SO_2 + M \rightarrow SO_3 + M$	1.4×10^{-42}
R(16)	$SO_3 + O + M \rightarrow SO_2 + O_2 + M$	8.0×10^{-39}
R(17)	$SO_3 + H_2O \rightarrow H_2SO_4$	6.0×10^{-24}

Table 4 OH radicals $DeSO_2$ reaction and the rate constants in liquid phase (Li, 1996)

No.	Reactions	Rate constants, $m^3/(mol \cdot s)$
R(18)	$HSO_3^- + OH \rightarrow H_2O + SO_3^- \rightarrow H_2SO_4 + e^-$	9.6×10^6
R(19)	$SO_3 + O_2 \cdot H_2O \rightarrow H_2O + SO_5^-$	1.5×10^6
R(20)	$SO_5^- + HSO_3^- \rightarrow HSO_4^- + SO_4^-$	75
R(21)	$SO_4^- + HSO_3^- \rightarrow SO_3^- + HSO_4^-$	2.0×10^6
R(22)	$SO_5^- + HSO_3^- \rightarrow HSO_5^- + SO_3^-$	25
R(23)	$SO_5^- + SO_5^- \rightarrow 2SO_4^- + O_2$	6.0×10^5
R(24)	$SO_3^- + SO_3^- \rightarrow S_2O_5^{2-}$	1.0×10^6
R(25)	$SO_5^- + SO_5^- \rightarrow S_2O_8^- + O_2$	1.4×10^5
R(26)	$SO_2 \cdot H_2O \rightarrow H^+ + HSO_3^-$	5.14 mol/m^3

These active radicals react with the SO_2 molecules and oxidize them into SO_3, the main mechanisms are shown in Table 3.

At the presence of ammonia, $(NH_4)_2SO_4$ will be finally formed. The by-products $(NH_4)_2SO_4$ particles can be collected by the precipitator and used as the fertilizer. Polluted flue gas is in this way treated and waste pollutant SO_2 treated is reused as a resource(Table 5).

Table 5 Reactions among sulfur oxide, sulfuric acid and ammonia

No.	Reactions
R(27)	$SO_3 + NH_3 + H_2O \rightarrow (NH_4)_2SO_4$
R(28)	$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$
R(29)	$2NH_3 + SO_2 + 2OH \rightarrow (NH_4)_2SO_4$

3 Conclusions

Under the condition of this experiment, the following conclusions can be drawn: (1) Water based radical injecting system can increase the number of HO, HO_2 and H_2O in the reactor. (2) The number of free radicals to increase with enhancing activation voltage and the number of water molecules.

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(Received for review November 18, 2002. Accepted April 21, 2003)